



Strong exciton bandwidth reduction in pentacene as a function of temperatureLukas Graf, Anncharlott Kusber, Bernd Büchner, and Martin Knupfer 
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The motion of excitons in organic semiconductors represents a key contribution to the performance of organic solar cells. It is determined by intermolecular exciton coupling. In momentum space, exciton coupling results in the exciton dispersion and defines the exciton bandwidth. We demonstrate that the exciton bandwidth in pentacene as measured using electron energy-loss spectroscopy is substantially temperature dependent, and it is drastically reduced going from 20 to 380 K. Following recent theoretical developments, we rationalize this reduction by a huge reduction of the (effective) charge carrier transfer integrals by about 60%. Our results indicate a strongly temperature-dependent energy transport in pentacene and related organic semiconductors.

DOI: [10.1103/PhysRevB.106.165429](https://doi.org/10.1103/PhysRevB.106.165429)**I. INTRODUCTION**

Organic semiconductor research and applications have evolved in previous years, and applications such as light-emitting diodes and organic photovoltaic cells have entered the market already [1–6]. The properties of such devices strongly depend on the photophysical behavior of the used organic semiconducting materials. Therefore, there is particular interest to fully understand the character of electronic excitations in organic semiconductors, which then allows one to model and predict the new materials' properties as well as device performances.

In the solid state, intermolecular interactions, which strongly depend on the molecular packing, play an important role in the determination of the photophysical behavior as well as of the energy and charge transport in organic semiconductors. Thus, these intermolecular interactions, including the transfer of charge, have been analyzed by state-of-the-art investigations in recent years, which predominantly have concentrated on model systems such as oligoacenes [7–30]. A key result of these studies is that a comprehensive understanding of the photophysics of the oligoacenes and other materials can only be achieved by the inclusion of charge-transfer (CT) excitons, which significantly mix with the molecular Frenkel excitons. The degree of mixing naturally depends on the energy difference of Frenkel and CT states, and very importantly, on the intermolecular transfer integrals of the involved orbitals, the highest occupied and the lowest unoccupied molecular orbital (HOMO and LUMO). For a number of cases, in particular also pentacene, it was shown that this Frenkel-CT mixing is more important for the nature and behavior of the lowest electronic excited states than the traditionally discussed Coulomb coupling of Frenkel states [21,31].

A key characteristic of excitons in crystalline materials is their dispersion or band structure $E(k)$, the dependence of the exciton energy E on the momentum or wave vector k . The total bandwidth of excitons in organic molecular materials

is dependent on the intermolecular coupling, which in most cases is largely dominated by next-nearest-neighbor interactions. In other words, the exciton bandwidth gives quantitative insight into this coupling. Moreover, it has been pointed out that the exciton bandwidth can provide information on the effective exciton mass (in the band limit) and the time evolution of an exciton wave package [32], has a direct consequence for the optical absorption profiles [21], and impacts the singlet fission matrix elements [30]. Also, the larger the exciton bandwidth, the more stable is the exciton delocalization with respect to static or dynamic disorder.

One of the most studied organic semiconducting materials certainly is pentacene. It has emerged as the archetypal system for detailed experimental and theoretical studies of charge-transfer exciton contributions to, e.g., optical absorption, singlet fission, or exciton dispersion [7,8,11–15,17,22,24,30,33–38]. In this paper, we demonstrate that the exciton bandwidth in pentacene as measured using electron energy-loss spectroscopy is significantly temperature dependent. Going from 20 to 380 K, it is substantially reduced. This can be rationalized by a reduced intermixing of Frenkel and charge-transfer excitons at high temperatures, i.e., a strongly temperature-dependent exciton coupling.

II. EXPERIMENT

All electronic excitation data have been obtained carrying out electron energy-loss spectroscopy (EELS) in transmission. This method is well suited to study electronic excitations as a function of momentum transfer in materials [39–45]. We have used a purpose-built spectrometer, which is described in detail elsewhere [46,47]. The kinetic energy of the incoming electrons is 172 keV, the beam size at the sample position is about 0.5 mm, and the total current of the direct beam behind the analyzer is about 3 nA (for further details, see Ref. [46]). The sample temperature can be chosen in the range of 20–380 K [46,47]. The energy and momentum resolution have been set to 85 meV and 0.035 \AA^{-1} , respectively. The EELS signal,

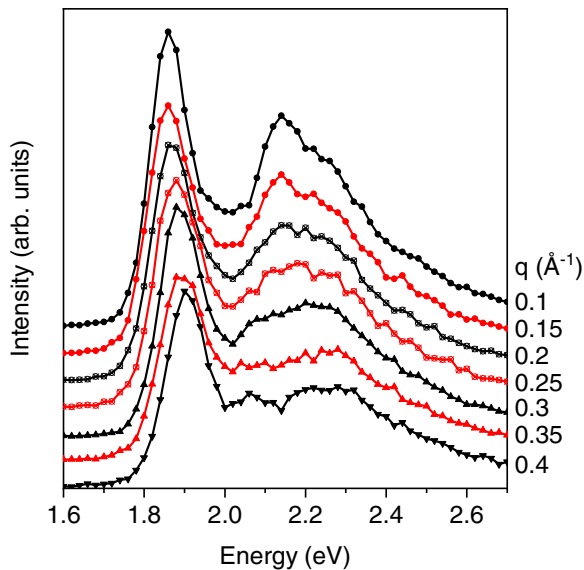


FIG. 1. Electronic excitation spectra of a pentacene thin film as a function of momentum transfer q as measured using electron energy-loss spectroscopy. The data have been taken at a 20 K sample temperature. For all data sets, see the Supplemental Material [53].

which is proportional to the loss function $\text{Im}[-1/\epsilon(\mathbf{q}, \omega)]$, was determined for various momentum transfers \mathbf{q} oriented in the film surface of the pentacene films. Electron diffraction data have been taken setting the energy loss to zero.

Thin films of pentacene (purchased from TCI GmbH) have been grown via physical vapor deposition onto single-crystalline KBr substrates kept at room temperature in a vacuum chamber, and the film thickness was about 100 nm. The pressure during deposition was 2×10^{-8} mbar, and the deposition rate as measured using a quartz microbalance was 1.5 nm/min. Under these conditions, it is reported that the so-called pentacene thin-film phase is formed [24,48–52]. This is confirmed for our films using electron diffraction, and all observed diffraction peaks agree well with this phase. Moreover, they show that the films grew in a (001) orientation, i.e., the film plane essentially represents the a, b plane of the crystal structure. For our EELS and diffraction studies, the films were floated off in distilled water, put on standard electron microscopy grids, and subsequently transferred into the spectrometer.

III. RESULTS AND DISCUSSION

We start the presentation of our results with the electronic excitation spectra of pentacene films measured using EELS at 20 K as depicted in Fig. 1. The data in Fig. 1 cover a momentum range up to 0.4 \AA^{-1} . Due to the predominant (001) orientation of the pentacene films our data represent an average of momentum directions in the a, b plane of the structure. However, a comparison with previous EELS and optical absorption data taken on single crystals [17,33,54] reveals that the curves in Fig. 1 to a large extent represent excitations for momentum (or polarization) vectors in the a crystal direction. This is not surprising if one takes into account that the excitation spectra for this direction are significantly more

intense [17,33,54], thus resulting in a -axis dominated thin-film data. The spectrum for the lowest momentum transfer of 0.1 \AA^{-1} shows a well-defined feature at about 1.86 eV, followed by a satellite structure, which is significantly different from that observed for individual pentacene molecules in solution [55]. Two additional features at about 2.14 and 2.26 eV can be observed, which demonstrates that exciton coupling in the solid state has a substantial impact on the spectral weight distribution in the excitation spectra of pentacene. Recent theoretical studies of the solid-state excitons in pentacene have shown that the complete excitation region can be quantitatively understood by a strong coupling of molecular Frenkel and charge-transfer (CT) excitons within a multiparticle basis set in addition to the vibronic coupling [7,17]. Also, it was demonstrated that the observed Davydov splitting in the polarization-dependent optical absorption data can only be understood based on the mentioned complex mixture of Frenkel, CT excitons, and vibrational states [7,17]. Figure 1 shows a strong intensity decrease around 2.2 eV with increasing momentum. This is related to the coupling of molecular Frenkel and CT excitons as described in Ref. [17], since the coupling matrix element is momentum dependent. Recently, an experimental analysis of the intensity variations in pentacene (and dibenzopentacene) single crystals confirmed this picture [56].

Considering the momentum dependence of the data in Fig. 1, a clear upshift can be observed for the lowest exciton feature. Again, this is in very good agreement with data from single crystals, where the momentum vector was oriented along the a crystal direction [54]. Moreover, the theoretical studies mentioned above have additionally provided a very good description of the exciton band structure in pentacene [17,54]. We have determined the energy positions of the lowest feature using a fit with a Gaussian profile and the energy shift going from 0.1 to 0.4 \AA^{-1} is 0.043 eV . This reproduces well what has been measured for single crystals [54], and we thus conclude that the data as obtained from thin pentacene films can be reliably used to study the exciton band dispersion in this material. We have not measured data for larger momentum values since then the exciton branch arising from the upper Davydov component becomes the energetically lowest band [54], which renders peak assignments ambiguous. As a consequence, the thin-film data directly provide us with only a part of the exciton bandwidth, but given the fact that the band has a cosinlike form [54], this can be extrapolated to obtain the full bandwidth. We also note that recent calculations indicate that there is virtually no difference in the exciton band structure for the thin-film and the single-crystal phase of pentacene [30]. Having established that the EELS data from pentacene films give a reliable measure of the exciton bandwidth, we present in Fig. 2 the temperature dependence of the corresponding spectra for momentum values of 0.1 and 0.4 \AA^{-1} . We start the discussion with the data at low momentum values which represent the optical limit. Clearly, the excitation spectra of pentacene change as a function of temperature. At 20 K the leading exciton feature has an energy position of 1.864 eV and shifts to higher energies, reaching an energy position of 1.947 eV at 380 K. Also, it broadens visibly going to higher temperatures. This parallels reports from temperature-dependent optical absorption

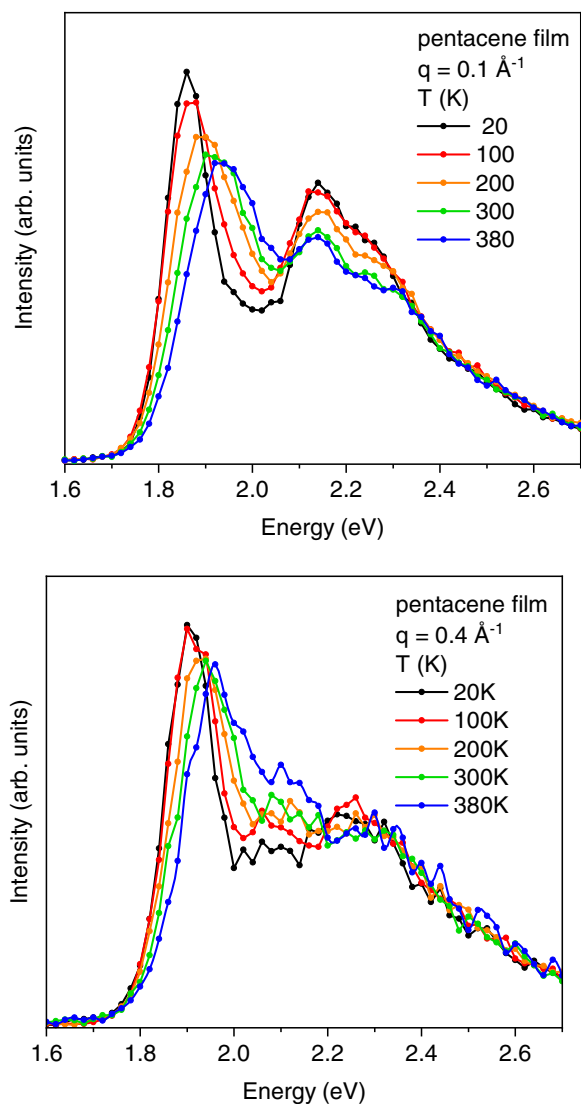


FIG. 2. Upper panel: Electronic excitation spectra of pentacene thin films at a momentum transfer of 0.1 \AA^{-1} as a function of temperature. Lower panel: Equivalent data at a momentum transfer of 0.4 \AA^{-1} .

studies of pentacene where small energy shifts to higher energy and spectral broadening have also been observed in various temperature ranges [33,52,57,58]. Moreover, different from the shift of the leading exciton feature, the main satellite at 2.14 eV stays constant in energy, which is also in agreement to what has been reported previously from optical absorption studies [33]. The data for 0.4 \AA^{-1} also show an upshift of the exciton feature, from 1.907 eV at 20 K to 1.96 eV at 380 K, smaller than for the lower momentum. In addition, some spectral broadening can also be observed.

The fact that spectral features become broader in energy as a function of increasing temperature is not surprising, as it reflects the decreasing lifetime due to enhanced scattering with vibrations. The energy shifts are more complex and a result of different contributions. In general, the energy positions of excitons in organic semiconductors are partly determined by a polarization contribution, which arises from the interaction of

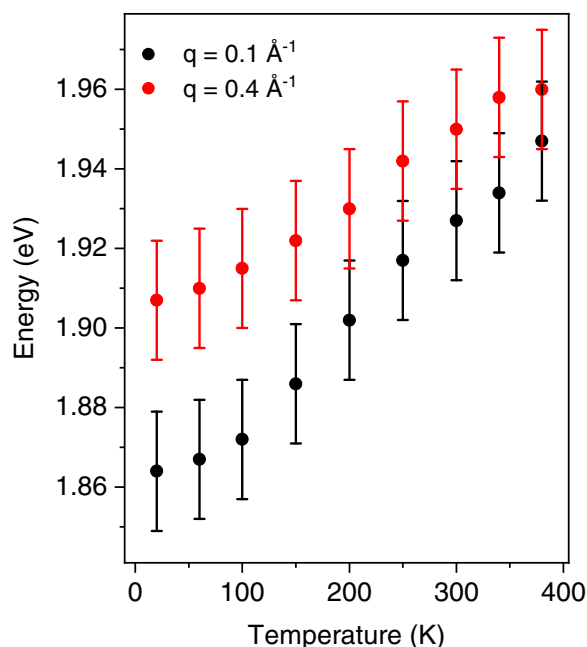


FIG. 3. Energy position of the lowest electronic excitation feature as seen in Fig. 2. These data demonstrate the reduction of the exciton bandwidth with increasing temperature in pentacene.

a molecule that is in the excited state with its neighbors in the ground state. This has also been termed the solution-to-crystal shift, and we expect it to be temperature dependent since the distances between the molecules change as a function of temperature due to thermal expansion [54,59], resulting in a small overall and momentum-independent energetic upshift of the exciton levels.

An important contribution to the exciton energy in pentacene is provided by intermolecular exciton coupling, which determines the exciton band structure [17]. To follow the temperature dependence of the exciton bandwidth, we present in Fig. 3 a summary of the energy changes as observed in our spectra above as a function of temperature. We have determined the energy positions as described in the Supplemental Material [53]. It becomes clear that the exciton bandwidth as represented by the difference of the exciton energies at $0.1\text{--}0.4 \text{ \AA}^{-1}$ is significantly reduced going to higher temperatures. These changes must have their origin in a temperature-dependent intermolecular coupling, and we will discuss this further based on a model Hamiltonian [17] which is able to provide a quantitative understanding of the optical data and the exciton bandwidth of pentacene. This detailed theoretical analysis of the excitons in pentacene has shown that intermolecular exciton coupling is essentially provided by charge-transfer processes, while the Coulomb coupling can be neglected [7,17]. Based on this model, the polarization dependence of the optical absorption data, the size of the Davydov splitting, and the exciton bandwidth all could be quantitatively rationalized. Moreover, it has been proposed that the essential physics of the lowest exciton band can be well described in a one-dimensional effective model with two molecules per unit cell and with inclusion of nearest-neighbor electron and hole transfer (t_e and t_h) integrals only [17]. These transfer integrals

allow for the charge-transfer coupling, and the lowest exciton band then is given by

$$E(k) = E_0 + \frac{E_{CT}}{2} - \sqrt{2(t_e^2 + t_h^2) + 4t_e t_h \cos(k/2) + \frac{E_{CT}^2}{4}}. \quad (1)$$

E_0 represents the exciton energy without coupling and E_{CT} is the energy difference of the intermixed charge-transfer state and E_0 . Inspection of Eq. (1) reveals that charge-transfer coupling results in two contributions to the exciton energy, a momentum-independent downshift and the momentum-dependent term causing the exciton bandwidth. Both depend on the transfer integrals t_e and t_h , but in a different manner. While the momentum-independent energy shift is given by $t_e^2 + t_h^2$, the exciton bandwidth is caused by the product $t_e t_h$, i.e., for a sizable exciton bandwidth both t_e and t_h must be large enough. This is true for pentacene, where various calculations reported a similar valence and conduction bandwidth, i.e., similar t_e and t_h [17,60–63], giving rise to an exciton bandwidth at a low temperature of about 110 meV [54]. The strong reduction of the exciton bandwidth signaled by our data indicates that these effective transfer integrals t_e and t_h are strongly reduced upon going to higher temperatures.

Previous experiments and calculations showed that the (effective) hole transfer integral in pentacene is significantly temperature dependent (see, e.g., Refs. [64–67]). This is caused by thermal expansion of the lattice, i.e., a smaller orbital overlap at higher temperatures, but also by relatively large thermal molecular motions, a consequence of the weak intermolecular van der Waals forces in molecular crystals. It is reasonable to assume that this is also the case for the electron transfer. Since it is the same charge-transfer integrals (t_e and t_h) which govern the exciton mixing and coupling in pentacene, it becomes clear that the strong reduction of the exciton bandwidth is of the same origin.

Motivated by the studies that provided similar electron and hole transfer integrals for pentacene, we continue our data analysis and discussion with the assumption $t_e = t_h = t$. In addition, we estimate the energy of the charge-transfer excitation E_{CT} to be 0.2 eV, as indicated by electroabsorption measurements [68] and the detailed theoretical analysis of the pentacene absorption spectra [17]. Based on these assumptions we now can translate the measured energy differences for $q = 0.1 \text{ \AA}^{-1}$ and $q = 0.4 \text{ \AA}^{-1}$ as depicted in Fig. 3 into an estimate for the effective transfer integral t at 20 and 380 K. To do so, we replace k in Eq. (1) with $2\pi q/a^*$, whereas $a^* = 1.05 \text{ \AA}^{-1}$ is the measured momentum value of the (100) Bragg peak. The energy differences (Fig. 3) are 43 meV at 20 K and 13 meV at 380 K, which gives us the effective transfer integrals $t_{20 \text{ K}} \approx 100 \text{ meV}$ and $t_{380 \text{ K}} \approx 40 \text{ meV}$. Thus, the transfer integral is reduced by about 60% going to high temperatures. We note that the low-temperature value $t = 100 \text{ meV}$ is quite close to theoretical calculations of the nearest-neighbor transfer integrals for holes and electrons [17]. A reduction of the transfer integrals on going to higher temperatures will also result in a shift to higher excitation energies of the lowest exciton as indicated by Eq. (1), in good qualitative agreement with the data in Fig. 2.

Thus, using the simplified one-dimensional description of the exciton dispersion in pentacene with intermolecular charge-transfer coupling provided by equal hole and electron effective transfer integrals, we can deduce that these transfer integrals are reduced by about 60% going from 20 to 380 K. This reduction of intermolecular exciton coupling now has consequences for the optical absorption and the photoluminescence (PL) properties. We expect that the Davydov splitting in the absorption spectra also becomes smaller at higher temperatures, which indeed has been reported previously [33,52]. Further, a larger exciton bandwidth at low temperatures may allow for a larger population of the band-bottom exciton state (at $k = 0$) after photoexcitation and relaxation. Then, the PL intensity should increase concomitantly, exactly what has been observed for pentacene [69].

IV. CONCLUSIONS

We have analyzed the exciton dispersion in pentacene films as a function of temperature using electron energy-loss spectroscopy on thin films. We show that thin-film data—although stemming from a polycrystalline sample—give a good measure of the exciton bandwidth of the lowest exciton feature in pentacene. Our data clearly demonstrate that the exciton bandwidth is strongly reduced going from 20 to 380 K. Taking into account recent achievements which showed that the intermolecular exciton coupling in pentacene is predominantly due to charge-transfer processes, we show that this exciton bandwidth reduction relates to a substantial temperature-dependent reduction of (effective) electron and hole transfer integrals. We suspect that (short-range) CT coupling of excitons is more strongly temperature dependent as compared to long-range Coulomb coupling, making the photophysics of CT coupled materials more temperature dependent. We emphasize that even at high temperatures the excitons in pentacene are charge-transfer coupled, as the corresponding Coulomb coupling is still much smaller [17]. The low-temperature exciton bandwidth of more than 100 meV indicates that the exciton wave function is well described by delocalized, Bloch-wave-like crystal states, which then also are less sensitive to local defects. This however will change going to higher temperatures, and we expect an increasing incoherent exciton transport upon increasing temperature. The microscopic origin of the reduction of the charge carrier transfer integrals is not clear yet. It can be related to enhanced phonon scattering at higher temperatures, but also to larger molecular distances due to thermal expansion. In the latter case, strain-dependent investigations could help to unravel this issue.

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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